

# Experimental study of the interaction between soot combustion and NH<sub>3</sub>-SCR reactivity over a Cu–Zeolite SDPF catalyst

Fabio Marchitti, Isabella Nova, Enrico Tronconi \*

Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, via La Masa 34, 20156 Milano, Italy

The interplay between the NH<sub>3</sub> SCR reactions and the oxidation of particulate matter (PM) is systematically investigated in view of the development of SDPF systems, which consist of a Selective Catalytic Reduction (SCR) catalyst coated on a diesel particulate filter (DPF). Both steady state and dynamic catalytic activity runs are performed on a commercial Cu-promoted zeolite catalyst supported on a SiC DPF crushed to powders and mixed with synthetic soot (Printex U). Three main effects are addressed, namely: (i) the influence of NO and/or NO<sub>2</sub> on soot combustion, (ii) the influence of the co-presence of NH<sub>3</sub> and NO<sub>x</sub> on soot combustion, and (iii) the influence of soot on the SCR reactions. It is found that NO<sub>2</sub> oxidizes soot to CO<sub>x</sub> at much lower temperatures than O<sub>2</sub>, but the co-presence of NH<sub>3</sub> strongly reduces such a downshift of the soot combustion light-off. In fact, our results clearly point out that the NH<sub>3</sub>-SCR reactions successfully compete with soot combustion for NO<sub>2</sub> usage, the reactivity with NH<sub>3</sub> being the NO<sub>2</sub> preferred reaction pathway at low temperature. In addition, the Standard and the Fast SCR reactions (NO<sub>2</sub>/NO<sub>x</sub> ≤ 1/2) are slightly but negatively affected by the presence of soot, while in case of NO<sub>2</sub> excess (NO<sub>2</sub>/NO<sub>x</sub> > 1/2) the SCR deNO<sub>x</sub> activity benefits from the soot/NO<sub>2</sub> interaction.

**Keywords:** SDPF, Soot combustion, Printex U, NH<sub>3</sub>-SCR, Cu–zeolite catalyst

## 1. Introduction

Diesel engines are extensively used for HD vehicles; more recently, they have become popular also for LD vehicles and passenger cars. This class of lean-burn engines is associated however with the emission of many pollutants in the exhaust gases, including NO<sub>x</sub>, particulate matter (PM), CO and hydrocarbons [1].

Nitrogen oxides is the generic term used for a group of highly reactive gases, which contain nitrogen and oxygen in different proportions [2]. NO<sub>x</sub> are primary pollutants, directly emitted from combustion processes. After their emission into the atmosphere, they are subjected to diffusion, transport and deposition phenomena. They can also give origin to new pollutant species, such as nitric acid (HNO<sub>3</sub>) and nitrous acid (HNO<sub>2</sub>), which are responsible for acid rains. Particulate matter (PM), or soot, is a complex heterogeneous carbonaceous framework with hundreds of different chemical compounds which are responsible for the soot's chemical and physical features [3–5]. The diesel soot shows a high intrinsic toxicity, which could be even amplified by other adsorbed

molecules: it is thus suspected to induce many health diseases, such as increased morbidity, cardiovascular and respiratory sickness, lung and bladder cancer [6–9].

On these bases, and also considering the increasing pressing emission regulations present in many countries, it is essential to put more efforts in the direction of developing new technologies to after-treat the lean exhausts from mobile sources (cars, trucks, trains and ferries).

In the field of simultaneous NO<sub>x</sub> and PM abatement, the SDPF system is one of the emerging technologies [10]. The SDPF system consists of an NH<sub>3</sub> Selective Catalytic Reduction (SCR) catalyst coated onto a wall-flow diesel particulate filter (DPF). Combining two functions in a single unit, it represents an effective solution for the limited volume available onboard of vehicles. Furthermore, SDPF devices can help during the cold start, enabling the SCR catalyst to reach the working temperature faster. They can ensure also an improved DPF regeneration, avoiding hot-spots formation along the monolithic substrate, since the presence of NO<sub>2</sub>, a better oxidizing agent than O<sub>2</sub>, promotes the soot combustion at lower temperature. It is well-known in the literature, however, that NO<sub>2</sub> plays an important role in the SCR reactions as well, as it enables the so called Fast-SCR reaction which increases the DeNO<sub>x</sub> activity in the low temperature region, typically below 250 °C [11].

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\* Corresponding author. Fax: +39 02 2399 8566.

E-mail address: [enrico.tronconi@polimi.it](mailto:enrico.tronconi@polimi.it) (E. Tronconi).

Although the SDPF technology relies on two well-established techniques (NH<sub>3</sub>/urea SCR and DPF), it is still controversial if and how the two chemistries affect each other. Undoubtedly, SCR reactions and soot oxidation proceed in different temperature ranges [10], but it is also worth remarking that the nature and the activity of the SCR coating and the specific soot features, together with the presence of promoting or inhibiting agents (e.g., NO<sub>2</sub> or hydrocarbons), can eventually result in some overlapping of their operating ranges. Indeed, it is nowadays well known [12,13] that NO<sub>2</sub> can provide additional and more effective reaction pathways to oxidize the soot ("passive regeneration").

In this context, a systematic work was carried out in our labs, focusing on three different fundamental aspects: (i) understanding the effect of the nature and composition of the oxidizing reaction environment on the soot combustion, (ii) clarifying how the simultaneous presence of NO<sub>x</sub> and NH<sub>3</sub> affects the PM combustion chemistry, and (iii) studying the impact of soot on the NH<sub>3</sub>-SCR chemistry, with focus on the key role played by NO<sub>2</sub>.

## 2. Experimental and methods

A commercial SDPF, based on a Cu-zeolite catalyst coated on a wall-flow SiC substrate, fully representative of the state-of-the-art SDPF technology, was tested in the form of powder. After removing the plugs at both ends, the original washcoated wall-flow monolith was crushed and sieved in order to obtain a grain size within the range 95–106 µm. The grain size was selected to prevent bypass, to mitigate pressure drop and to afford operation in a chemical regime.

In each SCR activity run, 70 mg of Cu-zeolite was mixed with 70 mg of cordierite as a diluent, and loaded in the flow-microreactor. In the case of combined SCR/soot oxidation runs, 50 mg of Cu-zeolite was mixed with 50 mg of cordierite and 5 mg of PrintexU (Degussa) according to a loose contact methodology [14–17]. PrintexU was used as synthetic model soot to ensure a high level of reproducibility and to avoid spurious influences due to: e.g., noble metal traces and/or VOC adsorbed on real engine soot. Moreover, the properties of PrintexU are well-known and available in the literature [14]. During each run, the whole load of PrintexU was completely burnt out, so that a new batch had to be loaded for the next run.

A flow-microreactor consisting of a quartz tube (6 mm i.d.) placed into an electric furnace was used in the experiments, with a thermocouple directly immersed in the powder bed to measure the reaction temperature. In order to directly compare the results, the two sets of experiments, with and without soot, were performed at different volumetric flows (172 and 241 Ncc/min, respectively) to ensure the same space velocity, defined as volumetric flow rate over Cu-zeolite catalyst load.

The reactor outlet was directly connected to three gas analyzers in a parallel configuration: a quadrupole mass spectrometer (Balzers QMS 200) for analysis of NH<sub>3</sub>, N<sub>2</sub>O, NO, NO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>O, a UV-Analyser (ABB LIMAS 11HW) for analysis of NO, NO<sub>2</sub>, NH<sub>3</sub>, and a Non Dispersive IR-Analyser (ABB URAS-14) for CO and CO<sub>2</sub> in parallel. NH<sub>3</sub>, NO, NO<sub>2</sub>, O<sub>2</sub> and He were dosed from cylinders with calibrated gas mixtures via mass flow controllers, while water vapor was added by means of a saturator. Kinetic runs included both isothermal steady-state experiments and temperature programmed reaction (TPR) experiments performed within the 150–500 °C and 150–700 °C T-ranges, respectively. In the case of the TPR runs the heating rate was slow (2 °C/min), resulting in quasi steady-state behavior: during diagnostic runs, the measured outlet concentrations were found overlapped with those of steady-state runs at each examined temperature. Typical feed concentrations of NO<sub>x</sub> (with 0 ≤ NO<sub>2</sub>/NO<sub>x</sub> ≤ 1) and NH<sub>3</sub> were 250 or 500 ppm, always

in the presence of O<sub>2</sub> (8% v/v) and H<sub>2</sub>O (5% v/v) and balance He. A more detailed description of the experimental rig and procedures can be found in Refs. [11,18,19].

For each run in which PrintexU was used, the C-balance was checked according to the following equation:

$$\text{Carbonbalance\%} = 100 \times \frac{\text{molCO}_x \times \text{CarbonMW}}{0.922 \times W_{\text{PrintexUloaded}}} \quad (\text{E.1})$$

where 0.922 represents the carbon weight fraction in PrintexU [14], and molCO<sub>x</sub> (CO + CO<sub>2</sub>) is the cumulative molar amount of CO<sub>x</sub> released during the TPR run, evaluated by integration of the CO<sub>x</sub> curves.

## 3. Results and discussion

### 3.1. Reference NH<sub>3</sub>-SCR activity runs

The NH<sub>3</sub>-SCR activity (without soot) was first evaluated, via steady-state runs, for the following, most representative reacting systems: NH<sub>3</sub> oxidation, Standard-SCR, Fast-SCR and NO<sub>2</sub>-SCR. Results are summarized in Fig. 1.

When feeding 500 ppm of ammonia in the presence of 5% v/v H<sub>2</sub>O and 8% v/v O<sub>2</sub> to the tested Cu-zeolite catalyst, Fig. 1A shows the onset of some oxidation activity around 250 °C and a full light off above 400 °C, in line with the NH<sub>3</sub> oxidation behavior of state-of-the-art Cu-promoted small-pore-zeolite catalysts [20]. Furthermore, a complete selectivity to N<sub>2</sub> in the whole temperature range was observed, according to:



Fig. 1B shows the results collected at Standard SCR conditions: 500 ppm of both NH<sub>3</sub> and NO were fed to the quartz microflow reactor with 5% v/v H<sub>2</sub>O and 8% v/v O<sub>2</sub>. The commercial Cu-zeolite powdered catalyst exhibits a high DeNO<sub>x</sub> activity, reaching complete NO and NH<sub>3</sub> conversions already at 250 °C. In the explored temperature range, N<sub>2</sub>O formation was below the detection limit of our analyzer (about 10 ppm). These results are in line with the occurrence primarily of the Standard SCR Reaction (R.2):

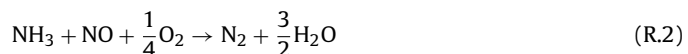
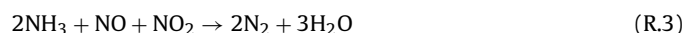


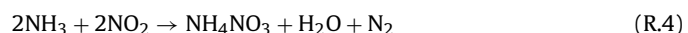
Fig. 1C shows the results collected at Fast SCR conditions, feeding 500 ppm of NH<sub>3</sub> and 250 ppm each of NO and NO<sub>2</sub> in the presence of H<sub>2</sub>O and O<sub>2</sub>. As expected [11,21], the Fast SCR reaction



proceeds already at very low temperature, with high conversions and N<sub>2</sub>-selectivities up to 500 °C.

In the case of the NO<sub>2</sub>-SCR conditions (results shown in Fig. 1D), only NH<sub>3</sub> and NO<sub>2</sub>, 500 ppm each, were fed to the reactor again in the presence of H<sub>2</sub>O and O<sub>2</sub>. In order to prevent severe ammonium nitrate build-up, the temperature steps started from 200 °C [22].

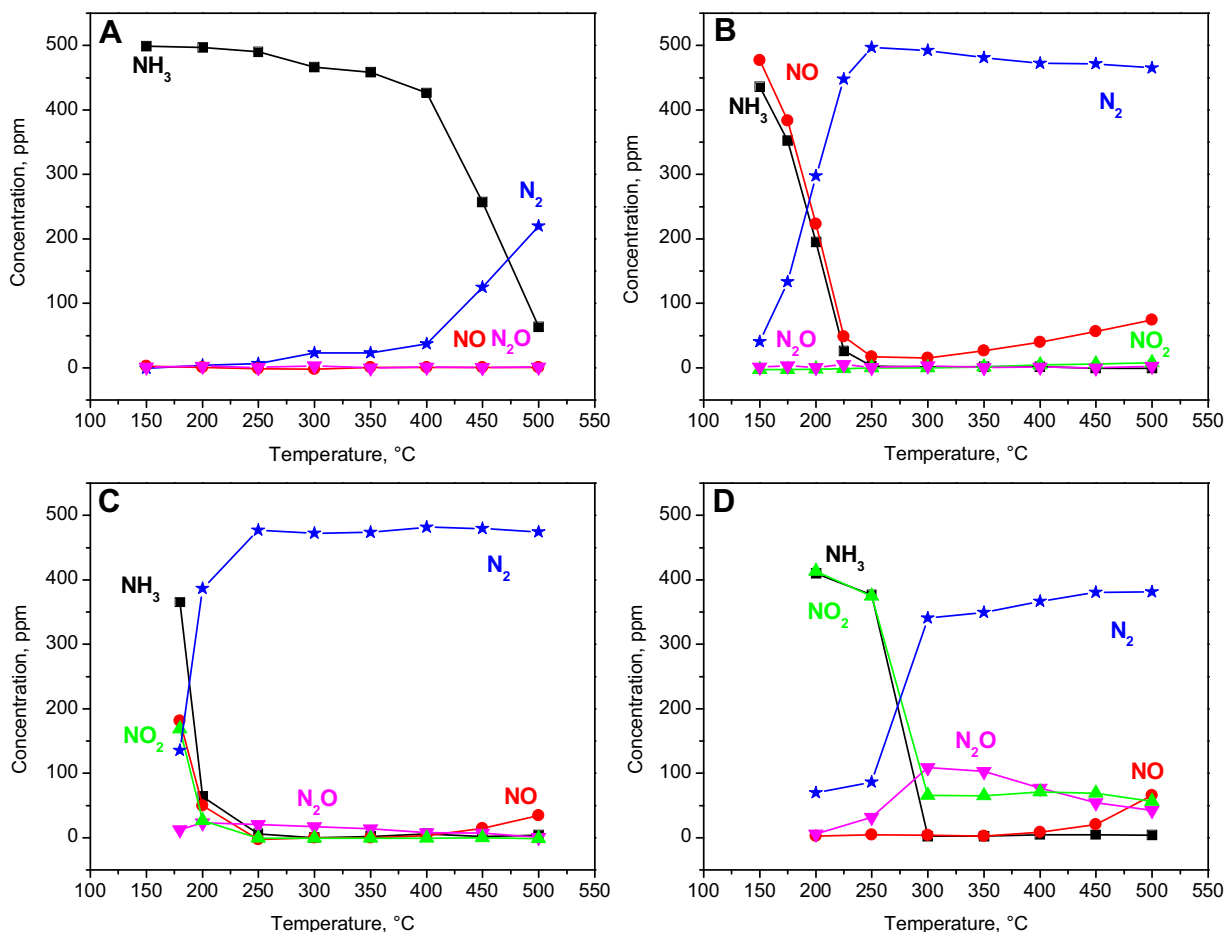
The equimolar consumption of ammonia and NO<sub>2</sub> visible between 200 and 250 °C indicates NH<sub>4</sub>NO<sub>3</sub> formation according to Reaction (R.4):



At temperatures higher than 200 °C ammonium nitrate is then decomposed to N<sub>2</sub>O. N<sub>2</sub>O formation reaches a maximum of 100 ppm at around 300 °C and then is gradually reduced to 40 ppm at 500 °C.

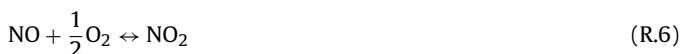
Above 250 °C, the NO<sub>2</sub>-SCR Reaction (R.5) suddenly becomes very active,





**Fig. 1.** SCR steady state runs. Flow rate = 241 cm<sup>3</sup>/min (STP), feed: H<sub>2</sub>O = 5%(v/v), O<sub>2</sub> = 8%(v/v), NH<sub>3</sub> = 500 ppm. (A) NO<sub>x</sub> = 0 ppm; (B) NO<sub>x</sub> = 500 ppm, NO<sub>2</sub>/NO<sub>x</sub> = 0; (C) NO<sub>x</sub> = 500 ppm, NO<sub>2</sub>/NO<sub>x</sub> = 0.5; (D) NO<sub>x</sub> = 500 ppm, NO<sub>2</sub>/NO<sub>x</sub> = 1.

converting the entire ammonia feed. Above 400 °C the NO<sub>2</sub> decomposition reaction produces a slip of NO according to Reaction (R.6) reverse:



### 3.2. Soot oxidation in the presence of NO<sub>x</sub>

The following step of the work consisted in the investigation of the soot combustion. For this purpose, oxidizing gas mixtures differing in both nature and amount of the oxidizing agents have been tested. Results are summarized in Fig. 2A–D.

At first, the simplest oxidizing agent was studied: 8% v/v O<sub>2</sub> in the presence of 5% v/v H<sub>2</sub>O and He as carrier gas was fed to the microflow reactor loaded with PrintexU mixed with the Cu–zeolite catalyst powders (Fig. 2A). On increasing the temperature from 150° to 700 °C, the PrintexU combustion was enabled according to the reactions below:

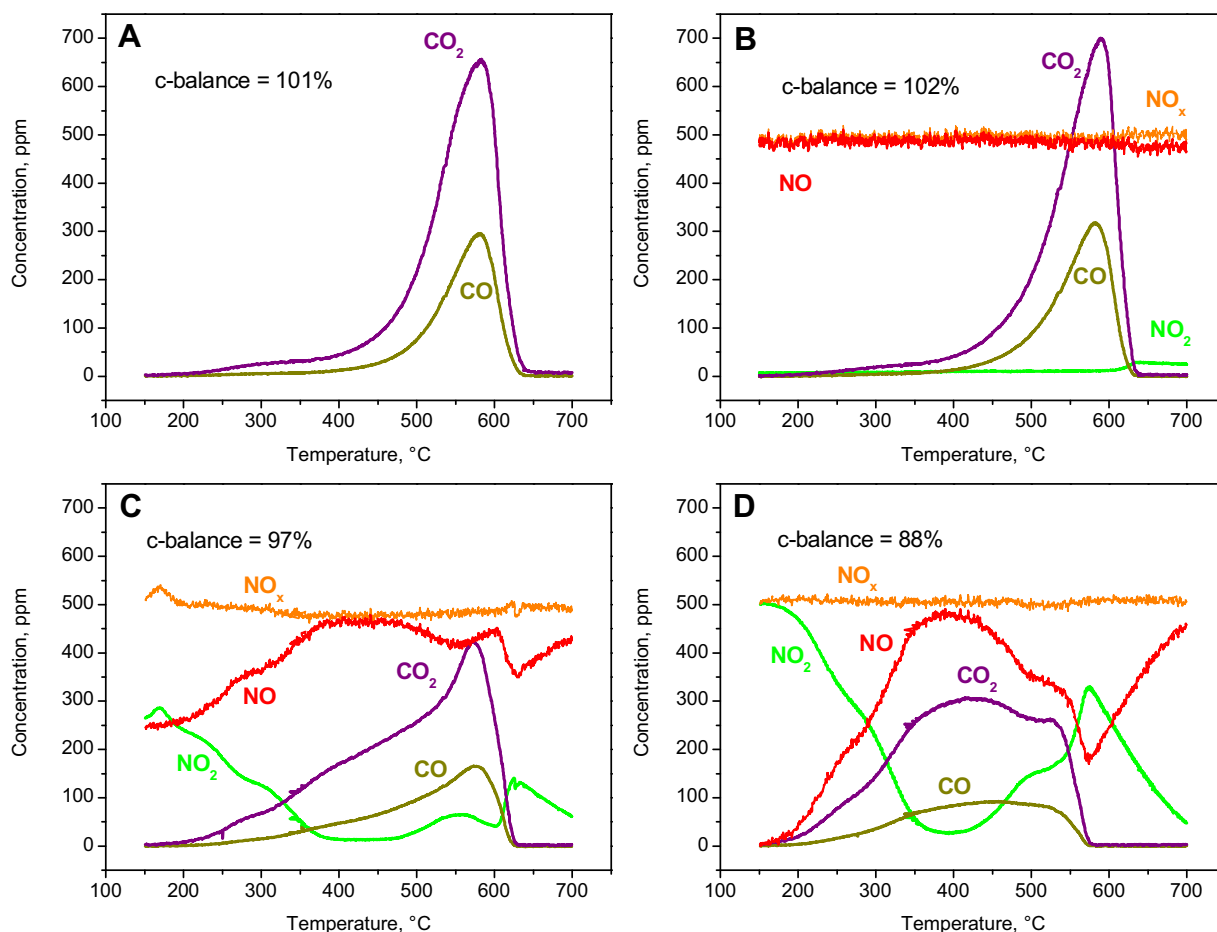


Indeed, as clearly apparent in Fig. 2A, CO<sub>2</sub> starts being produced around 250 °C, probably due to the presence of some volatile compounds in the soot, while the onset of CO production is detected at higher temperature. The CO<sub>x</sub> formation remains however quite limited below 450–500 °C, but at this temperature the full light-off of the soot combustion is achieved, Reactions (R.7) and (R.8) pro-

ducing large amounts of CO<sub>2</sub> and CO with a peak around 580 °C. Over the entire range of investigated temperatures CO<sub>2</sub> appears to be the main soot combustion product.

Subsequently, after reloading a new batch of PrintexU soot in the reactor mixed with the Cu–zeolite catalyst powders, the oxidation of soot by NO was addressed, feeding 500 ppm of NO with oxygen, water and He while the reactor was again heated up to 700 °C. The results, presented in Fig. 2B, show that the NO outlet concentration remained constant and equal to the feed value over the whole temperature range. It is also evident that, up to 450 °C, only a marginal CO and CO<sub>2</sub> evolution was detected. Starting from 450 °C a great CO<sub>x</sub> production was measured, with a maximum around 580 °C. The CO<sub>x</sub> curves in Fig. 2B are almost equal to those obtained when only oxygen was fed to the system (Fig. 2A); this clearly indicates that NO does not interact with soot even in the presence of the Cu–zeolite catalyst. We conclude that the effect of NO alone on soot combustion is essentially negligible in both the low and the high temperature range.

Next, soot combustion runs were carried out while feeding 250 ppm of NO and NO<sub>2</sub> (Fig. 2C). A strong effect was clearly apparent in this case, associated with a higher soot combustion activity in the low temperature region [16]. As a consequence of this boosted activity, evidently due to the co-presence of NO<sub>2</sub>, the light off temperature for soot combustion was shifted to 200–250 °C, roughly 100–150 °C lower than in the runs in Fig. 2A and B, carried out with oxygen and with NO/oxygen, respectively. Furthermore, the NO<sub>2</sub> consumption, which started around 200 °C, was associated with an



**Fig. 2.** PrintexU combustion runs in the presence of NOx. Flow rate = 172 cm<sup>3</sup>/min (STP), feed: H<sub>2</sub>O = 5%(v/v), O<sub>2</sub> = 8%(v/v). (A) NOx = 0 ppm; (B) NOx = 500 ppm, NO<sub>2</sub>/NOx = 0; (C) NOx = 500 ppm, NO<sub>2</sub>/NOx = 0.5; (D) NOx = 500 ppm, NO<sub>2</sub>/NOx = 1.

equivalent amount of released NO. The data are therefore in line with the following reactions:



wherein NO<sub>2</sub> oxidizes the soot to a CO/CO<sub>2</sub> mixture, while the nitrogen oxidation state is reduced from +4 in NO<sub>2</sub> to +2 in NO. To ensure that the NO released during the run is actually due to the PrintexU consumption, also the N-balance was estimated: as shown in Fig. 2C, the overall NOx remained constant and equal to 500 ppm during the whole run, confirming that NO directly comes from NO<sub>2</sub> reduction by soot. Fig. 2C also points out that, even in presence of 250 ppm of NO<sub>2</sub>, a COx peak is still evident at 580°C, that is related to soot combustion by O<sub>2</sub> as discussed above; indeed, at such high temperatures O<sub>2</sub> can effectively compete with NO<sub>2</sub> for the oxidation of the residual PrintexU still present in the reactor.

Fig. 2D illustrates the run performed feeding NO<sub>2</sub> only (500 ppm) in the presence of H<sub>2</sub>O and O<sub>2</sub>. Clearly, on doubling the NO<sub>2</sub> feed content there was a further benefit in the low temperature soot oxidation, which started already below 200°C and continued up to 570°C. In this case, however, the COx peak at 580°C due to soot oxidation by oxygen was not clearly evident, since the more effective soot removal by NO<sub>2</sub> at low temperature was able to complete the combustion of the carbonaceous species in the PrintexU [23] before oxygen became active. Remarkably, during the temperature ramp the NO<sub>2</sub> consumption was associated with an equivalent NO release, in line with Reactions (R.9) and (R.10). It is also worth noticing that at the end of the combustion process,

due to soot depletion (around 625°C and 575°C, respectively, in Figs. 2C–D), there was a slip of NO<sub>2</sub>, which partially decomposed to NO and O<sub>2</sub>.

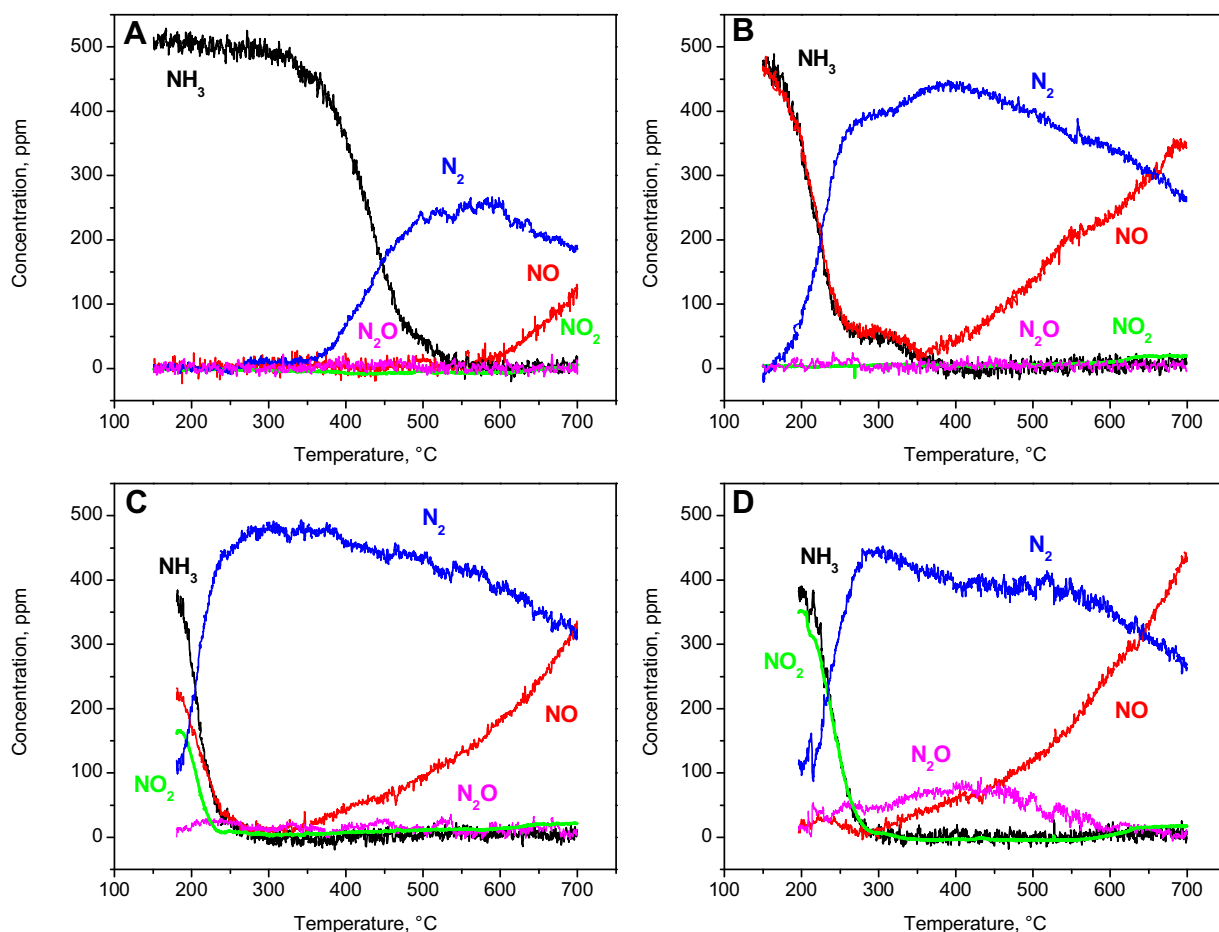
### 3.3. NH<sub>3</sub> + NOx SCR activity in the presence of soot

The third stage of the work addressed the effect of the soot on the NH<sub>3</sub>-SCR reactions. The data were obtained by carrying out quasi steady-state SCR activity runs (TPR = T-ramps with slow heating rate of 2K/min) on the commercial Cu-zeolite catalyst powders mixed with 10% w/w of PrintexU. Like for the previous cases, the H<sub>2</sub>O and O<sub>2</sub> feed concentrations were kept at 5% and 8%, respectively. The results are shown in Fig. 3A–D for each one of the four investigated reacting systems.

As illustrated in Fig. 3A, NH<sub>3</sub> oxidation started at 350°C, showing 100% selectivity to N<sub>2</sub> up to 550°C, while significant formation of NO was observed at high temperatures.

The Standard-SCR reaction (Fig. 3B) exhibited a full selectivity to N<sub>2</sub> together with a 1:1 NH<sub>3</sub>/NO molar conversion ratio up to 350°C. At higher temperatures the ammonia oxidation started to compete, being responsible for a slip of NO which increased with growing temperature, reaching 350 ppm at 700°C.

Even with PrintexU, the Fast-SCR (Fig. 3C) was the best performing SCR reaction, effecting a complete NOx removal already at 250°C with a very limited N<sub>2</sub>O formation. Above 350°C, again ammonia oxidation started to play an important role, determining a decrease in N<sub>2</sub> production, accompanied by substantial NO slip. It is important to highlight that below 250°C the 1:1 NO<sub>2</sub>/NO con-



**Fig. 3.** SCR runs in the presence of PrintexU. Flow rate = 172 cm<sup>3</sup>/min (STP), feed: H<sub>2</sub>O = 5%(v/v), O<sub>2</sub> = 8%(v/v), NH<sub>3</sub> = 500 ppm. (A) NO<sub>x</sub> = 0 ppm; (B) NO<sub>x</sub> = 500 ppm, NO<sub>2</sub>/NO<sub>x</sub> = 0; (C) NO<sub>x</sub> = 500 ppm, NO<sub>2</sub>/NO<sub>x</sub> = 0.5; (D) NO<sub>x</sub> = 500 ppm, NO<sub>2</sub>/NO<sub>x</sub> = 1.

sumption ratio typical of the Fast SCR reaction was not satisfied, NO<sub>2</sub> being converted in greater amounts.

The data in Fig. 3D reflect a typical NO<sub>2</sub>-SCR behavior in which both NH<sub>3</sub> and NO<sub>2</sub> were consumed by Reaction (R.4). Due to the excess of NO<sub>2</sub>, N<sub>2</sub>O formation was significant, with a maximum at 400 °C.

Fig. 4 shows the CO and CO<sub>2</sub> traces measured during the same SCR runs in the presence of soot presented in Fig. 3. During NH<sub>3</sub> oxidation and Standard-SCR experiments (Fig. 4A and B) there was a marginal CO–CO<sub>2</sub> production below 400 °C, while the soot oxidation by O<sub>2</sub> originated CO<sub>x</sub> peaks at 580 °C. In both cases, the soot combustion was quantitatively completed at temperatures around 640 °C.

Under Fast-SCR reacting conditions, when feeding 250 ppm of both NO and NO<sub>2</sub>, the CO<sub>2</sub> production was marginally increased (Fig. 4C) below 400 °C. Even though NO<sub>2</sub> was present, the combustion process was activated only at high temperatures generating the characteristic CO<sub>x</sub> peak at 580 °C.

Finally, Fig. 4D shows the results obtained under typical NO<sub>2</sub>-SCR conditions. Due to the excess of NO<sub>2</sub> fed to the reactor (500 ppm), the enhancement of the PrintexU combustion at low temperature was even more significant than in Fig. 4C, but again the amount of NO<sub>2</sub> was not sufficient to complete the process. Accordingly the O<sub>2</sub> combustion route, active at high temperature, eventually concluded the soot oxidation, resulting in the typical CO<sub>x</sub> peak at 580 °C.

### 3.4. Effect of soot on NH<sub>3</sub> + NO<sub>x</sub> SCR

Being the amount of the NH<sub>3</sub> stored onto the SCR catalyst one of the key factors for the NH<sub>3</sub>-SCR activity [20,24], a dedicated NH<sub>3</sub> adsorption + TPD run was performed first to evaluate the impact of soot. The estimate of the NH<sub>3</sub> storage capacity from the adsorption phase (not shown) (0.255 mmol<sub>NH3</sub>/g<sub>cat</sub>) was 10% higher in the case of Cu-Zeolite + PrintexU than for the clean Cu-zeolite (0.227 mmol<sub>NH3</sub>/g<sub>cat</sub>), indicating that PrintexU can adsorb NH<sub>3</sub>. In both runs, the isothermal adsorption phase was followed by TPD runs, which are displayed in Fig. 5. The analysis of the TPD curves points out that the additional ammonia adsorbed on soot is more strongly bonded to the soot surface than on the Cu-Zeolite, resulting in a shift of the NH<sub>3</sub> TPD peak to higher temperatures (Fig. 5). The acid sites [3], which could be produced by heating the soot in the presence of an oxidizing agent such as O<sub>2</sub>, are likely responsible for such a strong interaction between NH<sub>3</sub> and PrintexU.

To analyze the soot influence on the different SCR reacting systems, a direct comparison between the SCR reference data (Fig. 1) and PrintexU/SCR is presented in Fig. 6 in terms of NH<sub>3</sub> and NO<sub>x</sub> conversions. The results of the NH<sub>3</sub> oxidation runs carried out with and without PrintexU show (Fig. 6A) comparable NH<sub>3</sub> conversions up to 350 °C, but above this temperature the conversion in the run performed with PrintexU is 10–20% higher than in the baseline case. The higher activity is also confirmed by the N<sub>2</sub> traces (Figs. 1 A vs. 3 A), suggesting that the soot promotes the ammonia oxidation. A possible explanation could directly come from the nature of the



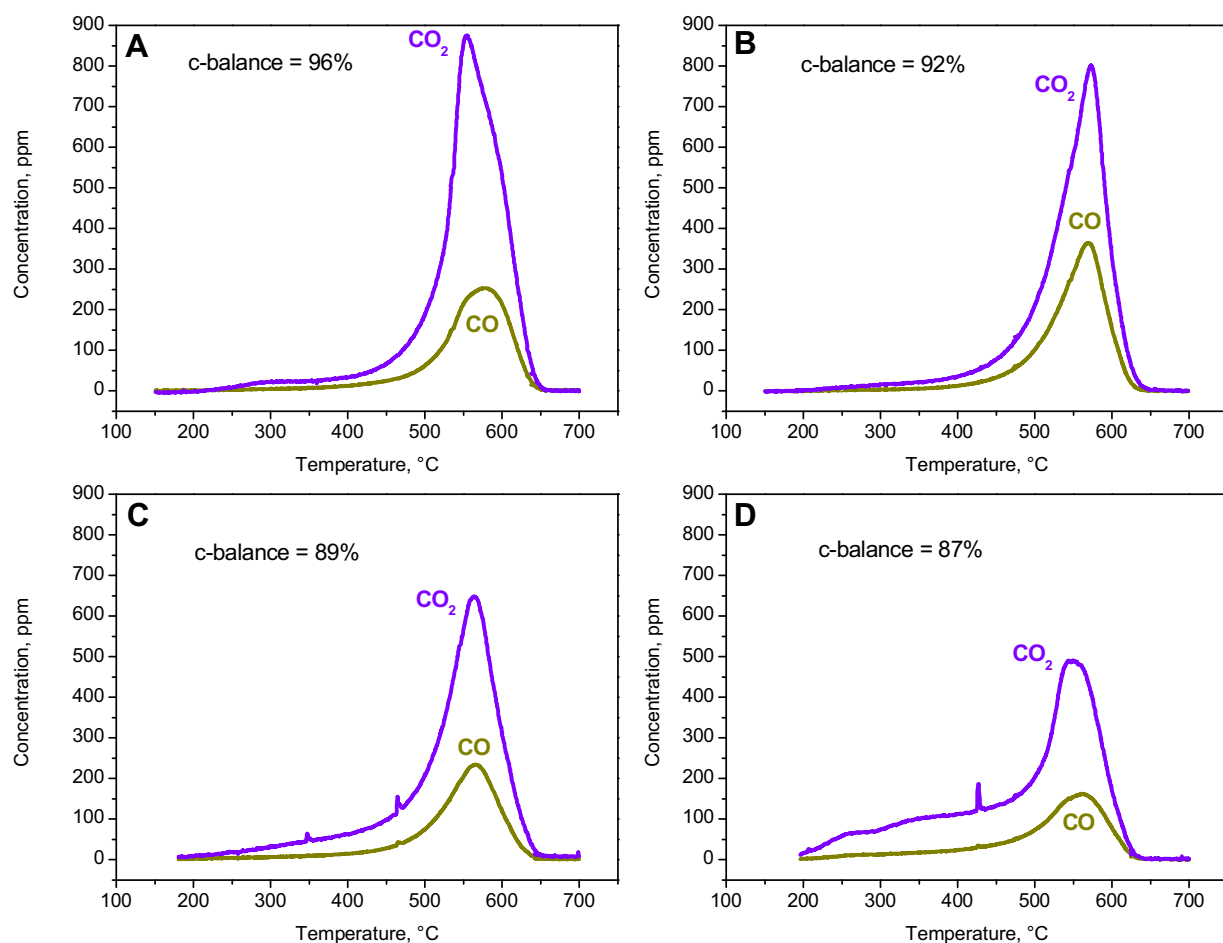


Fig. 4. PrintexU combustion runs under SCR reacting conditions (conditions as in Fig. 3).

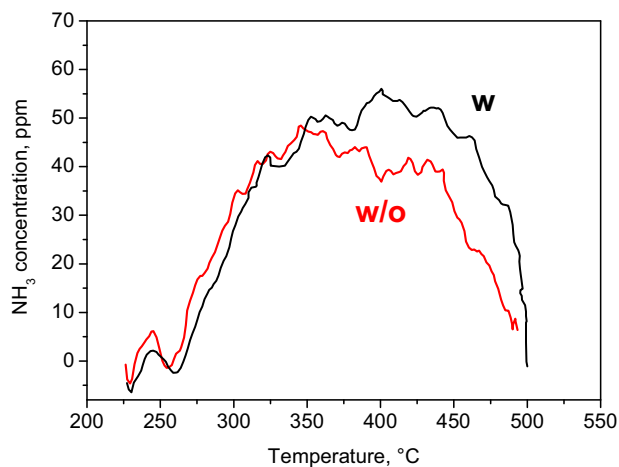


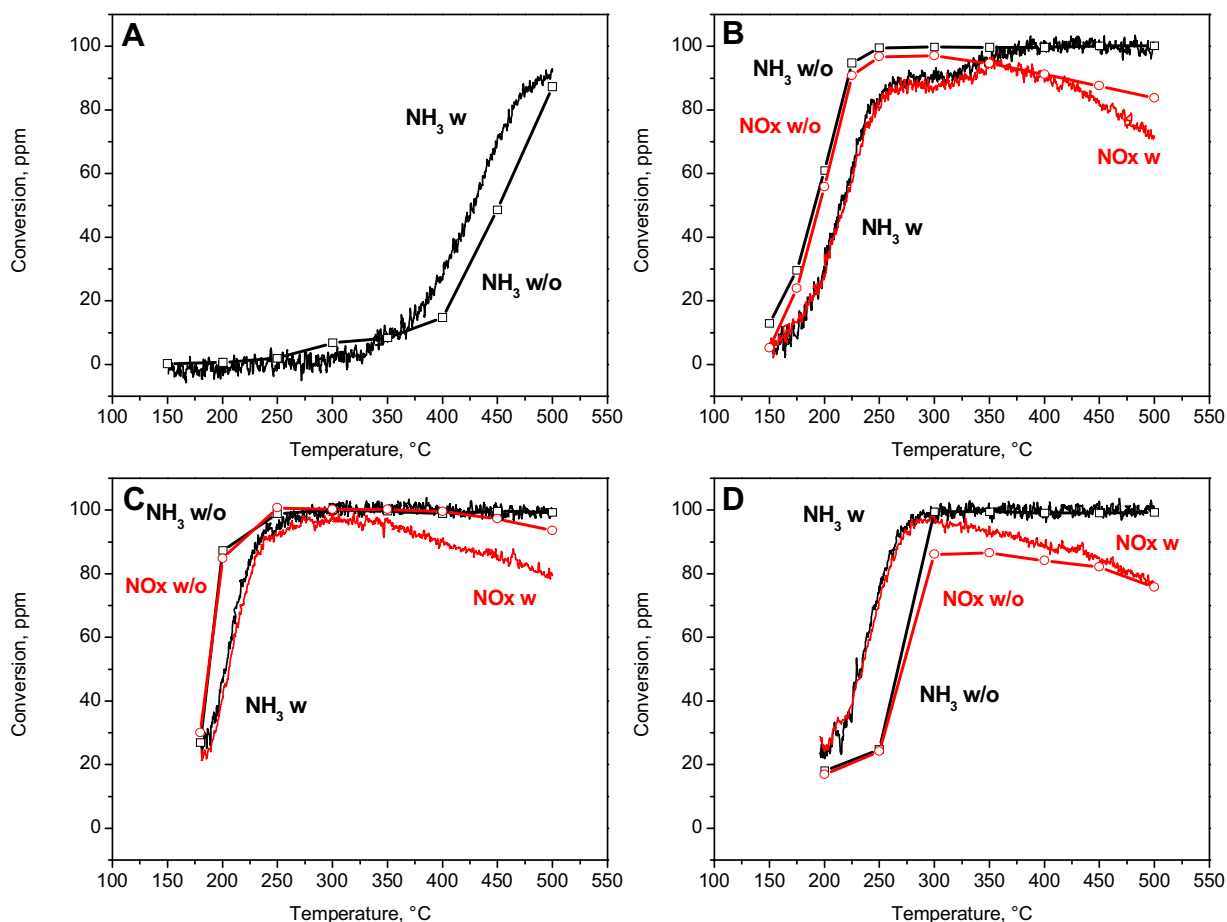
Fig. 5.  $\text{NH}_3$  evolution during TPD, after adsorption at  $T=150^\circ\text{C}$ . Flow rate =  $71\text{ cm}^3/\text{min}$  (STP),  $T$  ramp =  $15^\circ\text{C}/\text{min}$ , w = with PrintexU, w/o = without PrintexU.

soot used in this work. PrintexU is primarily a carbon framework ( $\sim 92\%$  content) with the addition of  $\text{O}_2$  and  $\text{H}_2$ :  $\text{O}_2$  may form oxygenated compounds and acid sites [25] in the PrintexU structure. The acid sites of the soot are responsible for the observed additional  $\text{NH}_3$  storage, while the oxygenated surface compounds could play a role in catalyzing the ammonia oxidation, since they can work as “activated oxygen donors” [3,26]. Such “donors” can also be formed by the gaseous  $\text{O}_2$  adsorbed on the soot surface [27]: this process

could be emphasized by the high surface area that characterizes PrintexU [3] improving the gas–solid contact.

Fig. 6B compares  $\text{NH}_3$  and  $\text{NO}_x$  conversions in Standard-SCR baseline runs and in Standard-SCR runs over the Cu–zeolite catalyst mixed with PrintexU. The presence of soot results in lower  $\text{NO}$  and  $\text{NH}_3$  consumptions at  $150\text{--}350^\circ\text{C}$ , which is the most interesting temperature range for Standard-SCR. Since it has been already demonstrated that co-feeding  $\text{NH}_3$  and  $\text{NO}$  has no effect on the soot combustion, and furthermore  $\text{NO}$  does not interact with PrintexU, a possible explanation for the observed inhibition could derive from an adverse effect of soot coverage on the Cu–zeolite active sites [28]. The facts that relatively large amounts of soot were loaded ( $10\% \text{ w/w}_{\text{cat}}$ ) in the microreactor, and that soot particles are three orders of magnitude smaller than the Cu catalytic powder [29], support this assumption. On the other hand, soot particles are still too big to block the pores of the zeolite support, the SCR reactions mainly occurring inside the zeolite framework structure. According to an alternative explanation, soot could compete with the SCR catalyst for  $\text{NH}_3$  adsorption, reducing the  $\text{NH}_3$  coverage on the Cu–zeolite. Nevertheless, our  $\text{NH}_3$ -TPD data suggest that soot just provides more (and stronger) ammonia adsorption sites in addition to those on the Cu–zeolite. Thus, it seems that more dedicated work is needed to fully clarify the physic-chemical reasons for the reduced SCR activity in the presence of soot.

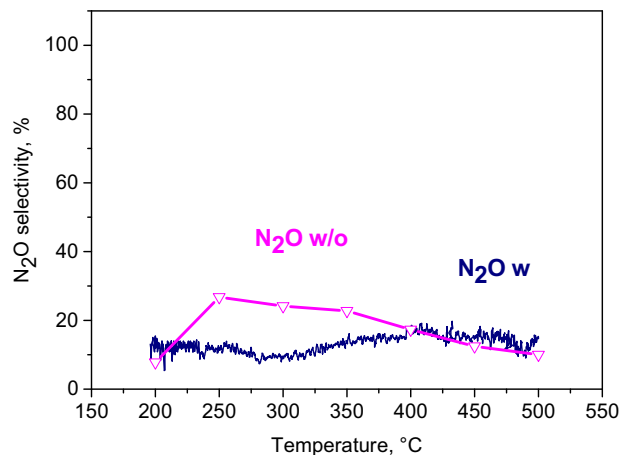
From Fig. 2C–D it is possible to conclude that  $\text{NO}_2$  is able to oxidize the PrintexU while being reduced to  $\text{NO}$  even at  $200^\circ\text{C}$ ; this high propensity to react with soot, in addition to the negative coverage effect proposed above, could be the reasons of the inhibition observed below  $300^\circ\text{C}$  when performing the Fast-SCR



**Fig. 6.** Effect of PrintexU on DeNOx efficiency (conditions as in Figs. 1 and 3): w = with PrintexU, w/o = without PrintexU.

reaction in the presence of soot (Fig. 6C). Support to this hypothesis directly comes from Fig. 3C, in which it is apparent that the equimolar NO/NO<sub>2</sub> ratio peculiar of the Fast-SCR was not respected; indeed, the PrintexU oxidation, Reactions (R.9) and (R.10), subtracts NO<sub>2</sub> otherwise available for the Fast-SCR reaction and prevents to achieve its optimal 1/2 NO<sub>2</sub>/NOx molar ratio.

As opposite to what was observed so far, when operating under NO<sub>2</sub>-SCR conditions (500 ppm of NH<sub>3</sub> and NO<sub>2</sub> with 8% and 5% of O<sub>2</sub> and H<sub>2</sub>O, respectively) a significant enhancement of both NH<sub>3</sub> and NOx conversions was observed (Fig. 6D). The promoting effect associated with the presence of the PrintexU is evident in a temperature range where both Standard-SCR and Fast-SCR are adversely affected by the presence of carbon black. It is a matter of fact that the NO<sub>2</sub>/NOx ratio strongly affects the catalyst DeNOx performance, since it governs the occurrence of different SCR reactions: Standard-SCR (NO<sub>2</sub>/NOx = 0), Fast-SCR (NO<sub>2</sub>/NOx = 1/2) and NO<sub>2</sub>-SCR (NO<sub>2</sub>/NOx = 1/1). Moreover, it is well-known that NO<sub>2</sub>-SCR is the slowest SCR reaction and the catalyst performance progressively increases while reducing the NO<sub>2</sub>/NOx ratio: the activity achieves a maximum at NO<sub>2</sub>/NOx molar ratio = 1/2, which corresponds to the Fast-SCR stoichiometry. Furthermore, it was shown that the NO<sub>2</sub>-SCR and PrintexU combustion can compete, at low temperature, for the NO<sub>2</sub> usage, ending up with a partial NO<sub>2</sub> consumption and NO generation associated with PrintexU oxidation. Thus, under NO<sub>2</sub> SCR conditions in the presence of soot, the soot-NO<sub>2</sub> reactivity shifts the actual NO<sub>2</sub>/NOx ratio from 1 to a value closer to 0.5, which is associated with a more effective DeNOx activity. In addition, as evident in Fig. 7, a further beneficial effect due to the presence of PrintexU, which moderately consumes NO<sub>2</sub>, is the

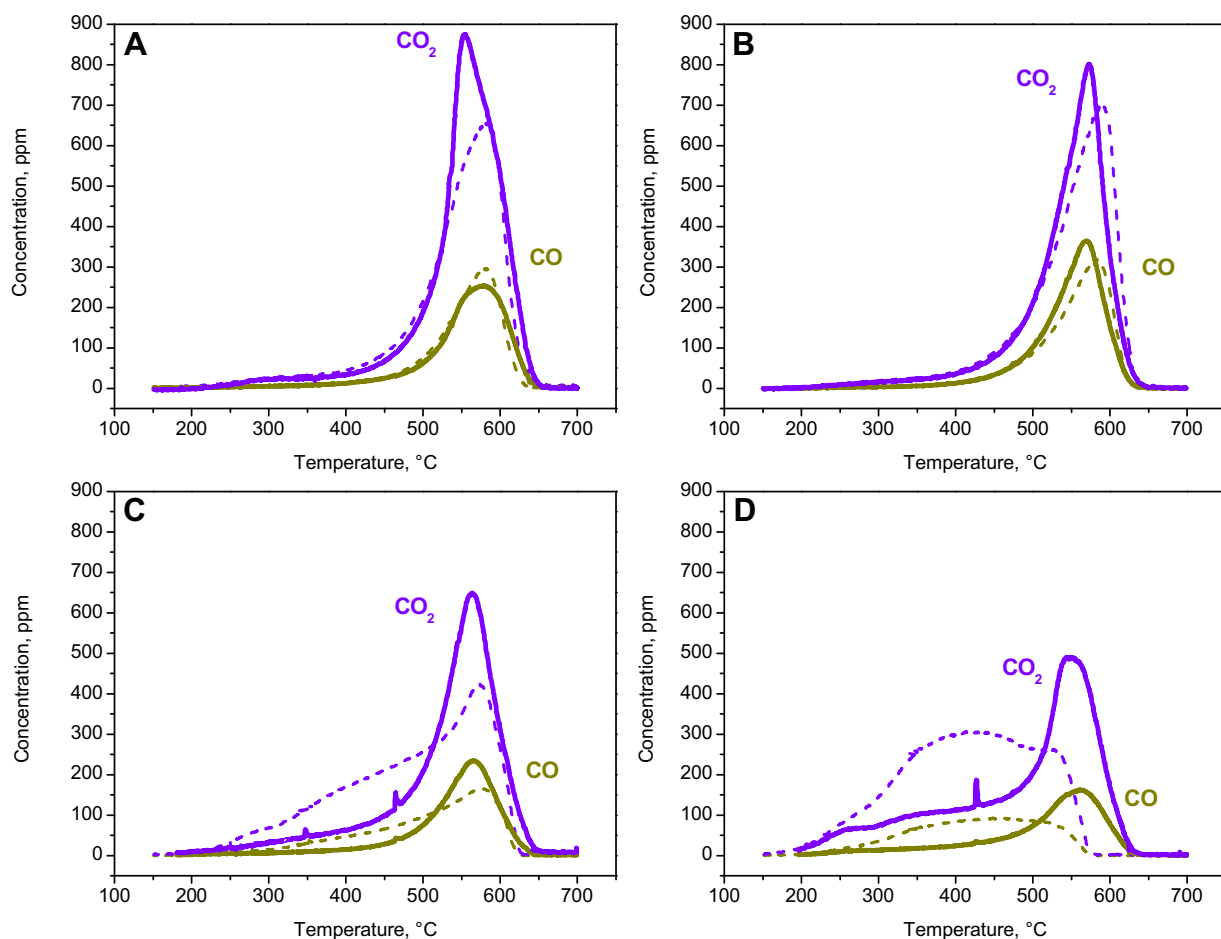


**Fig. 7.** Effect of PrintexU on N<sub>2</sub>O selectivity under NO<sub>2</sub>-SCR conditions (conditions as in Figs. 1 D and 3 D): w = with PrintexU, w/o = without PrintexU.

reduced selectivity to N<sub>2</sub>O at 250–400 °C. N<sub>2</sub>O formation in fact is correlated to a simultaneous excess of both NH<sub>3</sub> and NO<sub>2</sub> [11,30].

### 3.5. Effect of NH<sub>3</sub> + NOx on soot oxidation

The effect of the co-presence of NH<sub>3</sub> and NOx on the soot combustion was eventually investigated. Fig. 8 compares CO and CO<sub>2</sub> production in the experiments performed burning soot in the presence of NOx only (dashed lines, same results as in Fig. 2) and in those



**Fig. 8.** Effect of  $\text{NH}_3$  addition (500 ppm) on PrintexU combustion runs (conditions as in Figs. 2 and 4): solid lines = with  $\text{NH}_3$ , dashed lines = without  $\text{NH}_3$ .

performed burning soot in the presence of both  $\text{NO}_x$  and ammonia, with 500 ppm feed concentration (solid lines).

In Fig. 8A–B, related to the experiments performed in the presence of oxygen only, and  $\text{NO}$  and oxygen, respectively, the  $\text{CO}_x$  outlet concentration curves for runs with ammonia are almost overlapped to those without ammonia, but for a slight shift in the  $\text{CO}_x$  peaks toward lower temperatures. Notably, in these experiments two chemistries proceed in parallel, and compete for  $\text{O}_2$  usage, namely the PrintexU combustion by  $\text{O}_2$  Reactions (R.7) and (R.8) and some of the typical reactions proceeding in SCR converters, namely the  $\text{NH}_3$  oxidation Reaction (R.1) and the Standard SCR Reaction (R.2). The results in Fig. 8A and B show that the soot combustion is essentially unaffected by the presence of either  $\text{NO}$  or  $\text{NO} + \text{NH}_3$ , indicating that neither  $\text{NO}$  nor  $\text{NH}_3$  participate in soot combustion.

Fig. 8C shows the effect of ammonia on soot combustion in the presence of an equimolar mixture of  $\text{NO}$  and  $\text{NO}_2$ . Looking at the  $\text{CO}$  and  $\text{CO}_2$  profiles, it appears that the light off temperature for the soot combustion increases in the presence of ammonia, resulting in a clearly reduced  $\text{CO}_x$  production in the intermediate temperature range (250–500 °C). This behavior can be explained considering that the Fast-SCR Reaction (R.3) proceeds at these conditions, with  $\text{NH}_3$  reducing both  $\text{NO}$  and  $\text{NO}_2$  in equimolar proportion [31,32]. Thus, in the presence of  $\text{NH}_3$  Reaction (R.3) subtracts the  $\text{NO}_2$  otherwise available for the low temperature soot combustion according to Reactions (R.9) and (R.10). This suggests that the preferred reaction pathway for  $\text{NO}_2$  is the  $\text{NH}_3$ -SCR chemistry, rather than its reactivity with soot.

Fig. 8D shows the effect of ammonia on a run carried out with 500 ppm  $\text{NO}_2$  and  $\text{NH}_3$ , plus 5% of  $\text{H}_2\text{O}$  and 8% of  $\text{O}_2$ , in the feed stream. In the presence of ammonia (solid lines), the  $\text{CO}_x$  production due to soot combustion slowly increased from 200 °C up to 500 °C, which is the light-off temperature for the  $\text{O}_2$ -assisted soot oxidation: upon ignition, this oxidation lead to a 500 ppm peak of  $\text{CO}_2$  and a 175 ppm peak of  $\text{CO}$  between 550 and 580 °C. It is clearly evident from Fig. 8D that the presence of ammonia reduced the significant soot oxidation activity observed below 500 °C in the absence of ammonia (dashed lines), as in this temperature range  $\text{NO}_2$  reacted primarily with  $\text{NH}_3$  according to the  $\text{NO}_2$ -SCR pathway, Reaction (R.4) [32]. Thus, Fig. 8D confirms that the  $\text{NO}_2$ -activated soot combustion is adversely affected by the presence of ammonia, since  $\text{NO}_2$  preferentially reacts with  $\text{NH}_3$  to give  $\text{N}_2$  and  $\text{H}_2\text{O}$  according to the SCR chemistry.

#### 4. Conclusions

We have presented a systematic experimental study of the mutual interactions of  $\text{NH}_3$ -SCR and soot combustion over a Cu-zeolite catalyst from a coated SDPF device, using PrintexU as model soot. The study addresses three aspects related to the simultaneous  $\text{NO}_x$ -soot removal chemistries: (i) the effect of the nature and composition of the oxidizing reaction mixture on the soot combustion activity, (ii) the effect of the simultaneous presence of  $\text{NO}_x$  and  $\text{NH}_3$  on the soot combustion, and (iii) the impact of soot on the  $\text{NH}_3$ -SCR chemistry, with focus on the role played by  $\text{NO}_2$ .

After carrying out reference SCR activity runs, the impact of nature and composition of the  $\text{O}_2$ - $\text{NO}_x$  oxidizing mixture on the



PrintexU combustion was first studied. The results rule out any impact of NO on the combustion of soot, as no difference was noted when feeding either NO + O<sub>2</sub>/H<sub>2</sub>O or just O<sub>2</sub>/H<sub>2</sub>O. On the contrary, the presence of NO<sub>2</sub> is advantageous, since feeding 250 ppm of both NO<sub>2</sub> and NO + O<sub>2</sub>/H<sub>2</sub>O shifted the threshold temperature for the PrintexU combustion 100 °C lower than in the absence of NO<sub>2</sub>. The gain in the low temperature combustion activity was even greater when the NOx feed mixture included only NO<sub>2</sub>. In both runs involving NO<sub>2</sub>, NO<sub>2</sub> reacted with soot forming NO, thus keeping the total NOx balance constant.

When NH<sub>3</sub> was added to the same previously analyzed reacting systems, a negligible influence was detected on the PrintexU combustion in the absence of NO<sub>2</sub>. When simultaneously feeding NH<sub>3</sub> and NO<sub>2</sub>, however, the downshift of the PrintexU combustion light-off associated with the presence of NO<sub>2</sub> almost disappeared, indicating that the SCR reactions are the preferred reaction pathway for NO<sub>2</sub>. From a practical perspective, this implies of course that the passive regeneration of the soot-loaded filter effected by NO<sub>2</sub> from the upstream DOC will be substantially reduced in the SDPF configuration.

We have also found that PrintexU somewhat enhanced the ammonia oxidation, while both the Standard SCR and the Fast SCR activities suffered from the presence of PrintexU, resulting in a slight loss of DeNOx performance. On the opposite, the NO<sub>2</sub>-SCR activity benefited from the NO<sub>2</sub> reaction with soot at low temperature, which drives the NO<sub>2</sub>/NOx local molar ratio from unity down to a lower value closer to the optimal 1/2.

## References

- [1] H.-L. Chiang, Y.-M. Lai, S.-Y. Chang, *Atmos. Environ.* 47 (2012) 399–406.
- [2] D.L. Mauzerall, B. Sultan, N. Kim, D.F. Bradford, *Atmos. Environ.* 39 (2005) 2851–2866.
- [3] A. Setiabudi, M. Makkee, J.A. Moulijn, *Appl. Catal. B: Environ.* 50 (2004) 185–194.
- [4] V. Mugica, E. Ortiz, L. Molina, A. De Vizcaya-Ruiz, A. Nebot, R. Quintana, J. Aguilar, E. Alcántara, *Atmos. Environ.* 43 (2009) 5068–5074.
- [5] C.-H. Luo, W.-M. Lee, J.-J. Liaw, *J. Environ. Sci.* 21 (2009) 452–457.
- [6] J.L. Mauderly, *Zentralbl. Arbeitsmed. Arbeitsschutz Ergon.* 60 (2010) 412–417.
- [7] J.L. Mauderly, S. Seilkop, J.D. McDonald, A. Lund, M. Campen, *Am. J. Resp. Crit. Care* 183 (2011).
- [8] W. Zhang, T. Lei, Z.-Q. Lin, H.-S. Zhang, D.-F. Yang, Z.-G. Xi, J.-H. Chen, W. Wang, *Atmos. Environ.* 45 (2011) 1034–1041.
- [9] F.J. Kelly, J.C. Fussell, *Atmos. Environ.* 60 (2012) 504–526.
- [10] T.C. Watling, M.R. Ravenscroft, G. Avery, *Catal. Today* 188 (2012) 32–41.
- [11] M. Colombo, I. Nova, E. Tronconi, *Catal. Today* 151 (2010) 223–230.
- [12] F. Jacquot, V. Logie, J. Brilhac, P. Gilot, *Carbon* 40 (2002) 335–343.
- [13] B.R. Stanmore, V. Tschamber, J.F. Brilhac, *Fuel* 87 (2008) 131–146.
- [14] I. Atribak, A. Bueno-López, A. García-García, *Combust. Flame* 157 (2010) 2086–2094.
- [15] S. Jelles, B. Van Setten, M. Makkee, J. Moulijn, *Appl. Catal. B: Environ.* 21 (1999) 35–49.
- [16] R. Matarrese, L. Castoldi, L. Lietti, *Catal. Today* 197 (2012) 228–235.
- [17] J.P.A. Neeft, O.P. Van Pruissen, M. Makkee, J.A. Moulijn, *Appl. Catal. B: Environ.* 12 (1997) 21–31.
- [18] I. Nova, C. Ciardelli, E. Tronconi, D. Chatterjee, B. Bandl-Konrad, *AIChE J.* 52 (2006) 3222–3233.
- [19] D. Chatterjee, T. Burkhardt, M. Weibel, E. Tronconi, I. Nova, C. Ciardelli, *SAE Tech. Pap.* 01 (2006) 0468.
- [20] D. Wang, L. Zhang, J. Li, K. Kamasamudram, W.S. Epling, *Catal. Today* 231 (2014) 64–74.
- [21] P.S. Metkar, M.P. Harold, V. Balakotaiah, *Chem. Eng. Sci.* 87 (2013) 51–66.
- [22] M. Koebel, M. Elsener, G. Madia, *Ind. Eng. Chem. Res.* 40 (2001) 52–59.
- [23] N. Nejar, M. Makkee, M.J. Illan-Gomez, *Appl. Catal. B: Environ.* 75 (2007) 11–16.
- [24] I. Nova, C. Ciardelli, E. Tronconi, D. Chatterjee, B. Bandl-Konrad, *AIChE J.* 52 (2006) 3222–3233.
- [25] M. Mehring, M. Elsener, O. Kröcher, *ACS Catal.* 2 (2012) 1507–1518.
- [26] A. Setiabudi, M. Makkee, J.A. Moulijn, *Appl. Catal. B: Environ.* 42 (2003) 35–45.
- [27] M. Jeguirim, V. Tschamber, J.F. Brilhac, P. Ehrburger, *J. Anal. App. Pyrolysis* 72 (2004) 171–181.
- [28] S.Y. Park, K. Narayanaswamy, S.J. Schmiege, C.J. Rutland, *Ind. Eng. Chem. Res.* 51 (2012) 15582–15592.
- [29] K. Hinot, H. Burtcher, A. Weber, G. Kasper, *Appl. Catal. B: Environ.* 71 (2007) 271–278.
- [30] K. Kamasamudram, C. Henry, N. Currier, A. Yezerets, *SAE Int. J. Engines* (2012) 688–698.
- [31] M. Iwasaki, H. Shinjoh, *Appl. Catal. A: Gen.* 390 (2011) 71–77.
- [32] M. Colombo, I. Nova, E. Tronconi, *Catal. Today* 197 (2012) 243–255.